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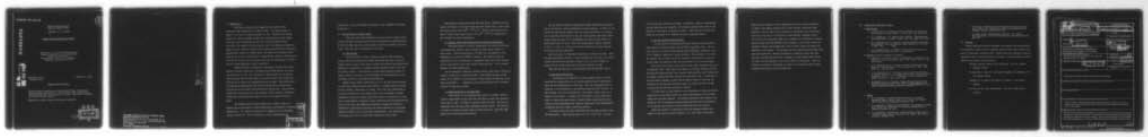

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Final Scientific Report*
Grant No. AFOSR-73-2493

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STANNIC OXIDE SEMICONDUCTOR STUDIES†

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Solid State Device
Research Group

February 15, 1978

FINAL SCIENTIFIC REPORT

†This research was supported by the Air Force Office of Scientific Research (AFSC) under Grant No. AFOSR-73-2493. The original title of this program was "Device Physics of Stannic Oxide and of Integrated Micro-Laser Optical Circuits".

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I. Introduction

This final technical report summaries the results of and activities under AFOSR Grant No. AFOSR-73-2493. This program began on March 15, 1973 and ran through December 31, 1976. However, work through January 31, 1978 is included in this report because work on this program is in fact still continuing, and will not really be complete until June 1978. The reason for this being that one of the graduate students who began his Ph.D. research ("Stannic Oxide Epitaxy and Field Effect Transistor Applications") under the original grant, was delayed by personnal circumstances, and is now in the process of completing his research, research which will achieve the last of the original goals set for this program, the fabrication of high temperature stannic oxide FET's.

During the first two periods of this grant, the title was "Device Physics of Stannic Oxide and of Integrated Micro-Laser Optical Circuits". The latter half of this title referred to a small portion of the program which involved work on diode pumps at 0.96 μm for solid state lasers suitable for use as sources for integrated optical systems. Work concentrated on studying Si-doped GaAsSb light emitting diodes and the results were reported in the literature (see Publications, Section III). The Air Force decided that this work was not their primary concern, however; alternative funding was obtained and after March 15, 1975 it was removed from this grant.

The primary thrust of this program was on stannic oxide, its physics and its potential for device applications, particularly at elevated temperatures. The results of this work are summarized in the following section, Section II. This is followed by a list of publications in

Section III, a list of personnel in Section IV, and a summary of coupling in Section V.

II. Device Physics of Stannic Oxide

There were five major divisions of the work done on stannic oxide: epitaxy; epilayer characterization and device application; thermoabsorption on the band edge; deep level spectroscopy; and electron emission from thin films. Each item will be discussed in turn below.

A. SnO_2 Epitaxy

The low pressure, chlorine transport chemical vapor deposition system originally developed under AFOSR sponsorship and used to grow the highest quality stannic oxide single crystals ever produced was substantially modified to incorporate a r-f heated, vertical epitaxy reactor and to permit epitaxy studies. The production of high quality epitaxial layers of stannic oxide is a key step in the development of high temperature active electronic devices in this wide band gap material.

Single crystal stannic oxide films up to 1.4 μm thick have been grown on <110> TiO_2 substrates without any evidence of thermal mismatch problems such as cracking, shattering, or crazing. With <110> TiO_2 established as a suitable substrate for SnO_2 epitaxy efforts are continuing to improve predeposition substrate surface properties, which it is hoped will in turn lead to improvements in epi-layer carrier mobilities (see following section). We have found that high temperature annealing in oxygen (5-30 hours at 1000-1100°C) significantly decreases the surface disorder of the polished substrates (LEED is used to make these observations). The crystallinity of the SnO_2 epi-layers is dramatically enhanced by this as well.

Both doped and undoped epi-layers have been grown. Antimony has been used as the dopant in the doped layers and these layers have, to date, been relatively heavily doped (10^{18} - 10^{19} cm^{-3}). Efforts are presently being made to reduce these doping levels to the 10^{16} - 10^{17} cm^{-3} range which is more suitable for device fabrication.

B. Epilayer Electrical Characterization and Device Application

Hall measurements of carrier concentration and electron mobilities on Sb-doped SnO_2 epitaxial layers confirm the high crystal quality of these layers. Electron mobilities of 80 cm^2/V-sec are measured at room temperature in layers with $10^{18} cm^{-3}$ carriers. This mobility value is approximately 60% of the mobility in comparably doped bulk single crystals, and is significantly better than previous epitaxial SnO_2. It is certainly adequate for device application.

We are preparing to fabricate Schottky barrier field effect transistors similar to those now so familiar in GaAs. Interestingly enough, our proposals to use SBFET's as active devices in SnO_2 predate the majority of the work on GaAs-FET's. Substantial work has already been done on Schottky barriers on SnO_2 bulk crystals.

C. Thermo-Absorption on the Band Edge

Measurements of the themoabsorption spectra of stannic oxide absorption edge between 20K and 115K have been made for both light polarizations, $E \perp c$ and $E \parallel c$. For $E \perp c$ two series of peaks are seen. The first is associated with the known direct forbidden excition series. The second is a series of relatively broader peaks and bumps above the absorption edge which has not previously been reported.

The new structure has been identified as being associated with absorption to the exciton levels accompanied by phonon emission. In order to correlate the known phonon energies with the excition positions, it is necesary to postulate the existence in SnO_2 of exciton-phonon quasi-bound states. We have shown that this is not unreasonable and that the SnO_2 lattice is sufficiently polar for this. With this interpretation, phonon "replicas" of the n = 1 line, n = 2 line, and continuum involving the three relevant LO phonons have been identified.

Little structure or temperature dependence is observed for $E \parallel c$. From the $E \parallel c$ observations, however, it was concluded that the onset of a direct-allowed transition was indicated at about 4.0 eV, or $\sim$0.4 eV higher in energy than the lowest energy direct-allowed transition for $E \perp c$.

This work has appeared in the literature (see Publications, item 2).

D. Deep Level Spectroscopy

The existence and importance of deep, mid-gap levels in stannic oxide has been demonstrated by our previous observations of visible blue-green and red photoluminescence from SnO_2. They will undoubtedly also be important to the performance of the depletion mode SnO_2 FET's as well. We have, however, very little information on the nature, origin, density, or energy of these levels. To supply this information, we have completed a study to characterize deep levels in stannic oxide using transcient capacitance-voltage measurements and thermally stimulated current measurements on Schottky barriers formed on bulk SnO_2 crystals.

Six energy levels have been identified; most were seen in both CV and TSC measurements. Their energies were 0.12, 0.17, 0.33, 0.47, 1.14 and

2.15 eV below the conduction band edge. In addition, capture cross-sections and trap densities were estimated, and tentative proposals were made of the identity of the defects producing the levels. These results have been presented in the thesis of J. Abrokwah and will be published shortly.

E. Electron Emission From Thin Films

In the course of investigating electron emission from SnO_2 films we have discovered intense emission from patterned In_2O_3/SnO_2 films. The pattern, etched in the films using standard photolithographic techniques, is an "H" or "dumbbell" shape with a narrow crossbar. With crossbars 0.1 mm wide we typically see in excess of 0.5 mA of emission current with a current of 15 mA through the sample and 300 V on the collector (2 cm from the sample).

This is the first work of this nature on SnO_2 films containing In_2O_3 and on sputtered films. Other work we are aware of on similar emitters has used pyrolytically deposited SnO_2 films (usually involving $SnCl_4$ and Sb doping) and the highest reported emission currents have been below 1 mA. In addition to the much higher emission, we have seen as high as 10 mA, we find that the parameters of the sputtered films are easier to control and that the high In concentration films are very easy to pattern.

In recent work on these emitters we have attempted to refine the emitter shape and the contacting procedure but these "improvements" have decreased rather than increased emission. The emission mechanism itself appears to be thermionic and the intense localized heating associated with the operation of the emitters then leads to eventual deterioration of the devices.

While the concept of a patterned, thin-film thermionic emitter has appeal for application in panel displays, it is clear that a much larger

effort will be required to fully understand all of the critical parameters in these or any similar emitters and to fully evaluate and realize their potential. We feel that a better approach to realizing a thin film emitter array is to not rely on a fortuitous but unpredictable "forming" process as is done in the In_2O_3/SnO_2 films but to instead try to fabricate an emitter directly using thin film materials and techniques. In our work a thin film thermionic emitter was designed which used a thin Mo film as the heater and (BaSrCa)O as the emitter. The structure has been analyzed and prototype units have been fabricated. Several microamperes of emission current have been obtained from these devices which is adequate for many display applications. The major problem remaining is the turn-on speed of the devices. This can perhaps be overcome by suspending the heater in the emitting region thereby thermally insulating it from the substrate.

III. Publications, Abstracts, Theses

A. Publications

1. S. Samson and C. G. Fonstad, "Defect Structure and Electronic Donor Levels in Stannic Oxide," J. Appl. Phys., 44, 4618(1973).

2. R. D. McRoberts, C. G. Fonstad, and D. Hubert, "Thermo-absorption Measurements on Stannic Oxide," Phys. Rev. B10, 5213 (1974).

3. S. K. Brierley and C. G. Fonstad," Silicon Doped Gallium Arsenide Antimonide Electroluminescent Diodes Emitting to 1.06 μm", J. Appl. Phys., (1975).

4. J. K. Abrokwah and C. G. Fonstad, "Deep Level Spectroscopy on Stannic Oxide Single Crystals", in preparation.

B. Abstracts (papers presented at meetings)

1. C. Rieck, C. G. Fonstad, and M. S. Dresselhaus, "Dielectric Constants for SnO_2 and Tetragonal GeO_2," Bull. Amer. Phys. Soc. 17, 1419 (1973).

2. R. D. McRoberts and C. G. Fonstad, "Thermally Modulated Transmission of Stannic Oxide at the Absorption Edge," Bull. Amer. Phys. Soc., 19 308 (1974).

3. S. K. Brierley and C. G. Fonstad, "Growth and Characterization of Silicon Doped $GaAs_{1-x}Sb_x$ Luminescent Diodes," IEEE Specialists Conference on the Technology of Electroluminescent Diodes, Atlanta, GA, Nov. 20-21, 1975..

4. M. Hartwell and C. G. Fonstad, "Strong Electron Emission from Patterned Tin-Indiom Oxide Thin Films" in Proceedings of the 1975 International Electron Devices Conference (IEEE, N.Y., 1975)

C. Theses

1. R. D. McRoberts, "Thermal Modulation Study of the Optical Absorption Edge of Stannic Oxide," M.S. Thesis, MIT, Department of Electrical Engineering, February, 1974.

2. S. K. Brierley, "Emission Tailored GaAsSb: Si Luminescent Diodes" M.S. Thesis, MIT, Department of Electrical Engineering and Computer Science, May 1975.

3. J. K. Abrokwah, "Spectroscopy of Deep Extrinsic Energy Levels in Stannic Oxide Schottky Barriers," M.S. Thesis, MIT, Dept. of E.E.C.S., February 1976.

4. P. Norris, "Epitaxial Stannic Oxide and Device Applications," Ph.D. Thesis, MIT, Department of Electrical Engineering and Computer Science, expected June 1978.

5. L. Wong, "A Thin Film Thermionic Emitter", M.S. Thesis, MIT, Department of Electrical Engineering and Computer Science, May 1977.

IV. Coupling

Primary coupling activities throughout the program---and coupling which is continuing to date---involve supplying stannic oxide single crystal speciments to researchers requesting them. Samples have been supplied to numerous individuals both in the United States and abroad. Several examples and their specific applications are listed below:

Professor Laperye, Montana State University - for use in photoemission studies.

Dr. Mortimer H. Zinn, U.S. Army System Command, Fort Monmouth, N.J. - for surface studies.

Professor W. E. Spicer, University of Illinois -- for surface studies.

Mr. Chun Lim Lau, Bell Laboratories - for use in ESCA studies of SnO_2.

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Stannic oxide; wide bandgap semiconductors; device physics; electron emission; deep level spectroscopy; chemical vapor deposition; epilayer; FETs; thin films

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

High quality stannic oxide epilayers were grown in TiO_2 substrates without evidence of thermal mismatch. Electrical characterization was performed and device applications were studied. Stannic oxide appears to be suitable for high temperature microwave Schottky barrier field effect transistors.

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